# The influence of the environment factors and the surface treatment on Stress Corrosion Cracking of Type 304 Austenitic Stainless Steel

Nguyen Thi Thanh Nga[1], Le Thi Hong Lien[2], Tadashi Shinohara[3]

[1]Institute of Material Science – Vietnam Academy of Science and Technology (IMS/VAST)
[2]Institute of Material Science – Vietnam Academy of Science and Technology (IMS/VAST)
[3]National Institute for Material Science - Japan

***Abstract***— *The aim of this work is to understand the combined effects of stress, temperature, humidity and chloride ion on the susceptibility of stress corrosion cracking (SCC) of type 304 austenitic stainless steel. The occurrence of SCC was investigated using the as received (cold work), sensitized samples those are exposed to the environmental test chamber at 40$^o$C and 70$^o$C, respectively. The humidity from 40% to 70% RH with gradient of 10% was applied during the corrosion test lasted 720h. The results showed the environmental conditions where SCC crack can be occurred and where it can be avoided. The initiation and the propagating of SCC crack on the flat and U-bend specimens were grown up to correspond to the increasing of test temperature. Very high stress corrosion cracking can be observed in the period of low relative humidity (40%) and temperature (40$^o$C).*

***Keywords— SCC, austenitic, cold work, sensitized, chloride ion.***

## I. INTRODUCTION

Stress Corrosion Cracking (SCC) is a common, often dramatic failure mode for many austenitic stainless steel systems. SCC occurs via a combination of three critical factors: a tensile stress (which can be applied and/or residual), a specific corrosive environment and a susceptible material [1,2]. During the past decade, a consensus had been reached about stress corrosion cracking starting from pits on the smooth samples [3,4]. The general assumption was that SCC, including Atmospheric Induced Stress Corrosion Cracking (AISCC), of austenitic stainless steels does not occur at temperature below the critical temperature, for example 50$^o$C for type 304 stainless steel [5]. So far, it has been proven incorrect. The studies of H.E. Hannien et al. in 1979 [6], which performed SCC test using stainless steel U-bend specimens fabricated according to ASTM standard G30-97, showed that the SCC initiation was observed on the specimens deposited with simulated sea salt and exposed to the environmental test chamber at the temperatures between 35 and 52$^o$C. The amount of salt deposited on the specimen surfaces were between 0.1 and 10 g/m$^2$. In 2008, Tani et al. showed that there was measurable Trans-Granular Stress Corrosion Cracking (TGSCC) at the temperature of 298K but it was not clear whether this was a true threshold or whether cracking could have been seen at low temperature in longer experiments [7]. Recent published work by Phan and Cook et al. has observed AISCC at temperatures as low as 40$^o$C of the U-bend specimens of parent material from the surface deposited with salt particles exposed to a humid atmosphere [8,9]. This work described a series of test to evaluate systematically the effect of relative humidity (RH) and concentration of chloride ion deposited on the surface of 304 and 316 austenitic stainless steel samples on SCC initiation at low temperature. It was suggested that the SCC susceptibility of the stainless steel samples was both relating to the process of deliquescence and the increasing of RH. SCC cracks propagate most often by inter-granular path which is more common rather than trans-granular path in austenitic stainless steels.

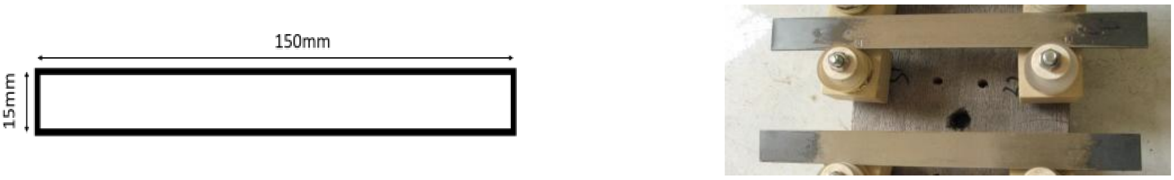
This work described a series of test in order to systematically evaluate the effect of tensile stress, relative humidity and chloride ion of which SUS 304 with suffering on SCC initiation at 40$^o$C and 70$^o$C. The distribution of cracks and the tree branch cracks were well presented.

## II. MATERIAL AND METHOD

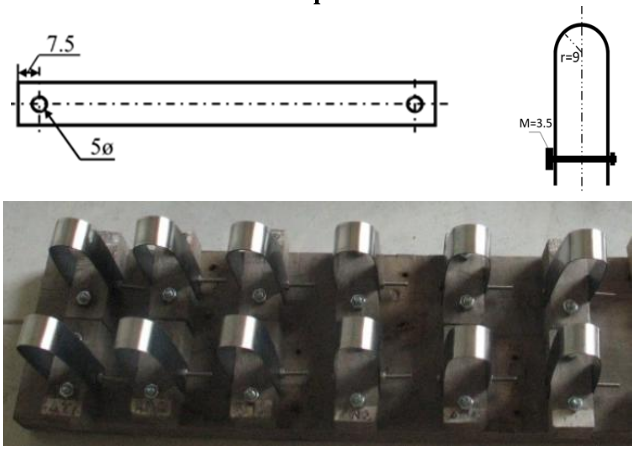
### 2.1 Material and specimens

Type 304 austenitic stainless steels (0.065C, 0.58Si, 1.9Mn, 0.014P, 0.022S, 8.789Ni, 18.56Cr, %mass, Fe: bal) with thickness of 0.8mm was cut into 15mm x150mm as the samples. The tests were carried out using the flat and U-bend specimens fabricated from the above steel (Fig.1).

The testing samples were kept in the condition of "as - received (cold-worked)" and "sensitized". For the sensitized condition, the samples were treated at 700$^o$C for 2 hours, after that, they were cooled down slowly in the air. The U-bend specimens were prepared according to ASTM G30-97 [10].




**a/ Flat specimen**




**b/ U-bend specimen**

**FIGURE 1. Flat (a) and U-bend (b) specimens**

Prior to fabrication the metal strips were abraded to 1200 grit with silicon carbide paper and thoroughly cleaned in distilled water to remove the surface contaminations and then dried in acetone. All of the specimens were inspected under a microscope at 40 times magnification to ensure that no crack or fissures were presented before testing.

### 2.2 Salt deposition and exposure method

Both flat and U-bend samples were dropped with six droplets of chloride solution as shown in Fig.2. For the U-bend samples, two big drops were deposited on the top area and four smaller ones on the side area.

**FIGURE 2. U-bend specimen with freshly deposited droplets**

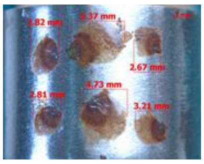
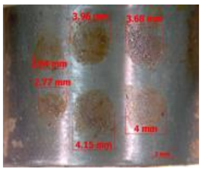
NaCl and $MgCl_2$ solutions which are saturated and diluted were used to deposit on the samples. The content of chloride ion in $gCl^-/m^2$ were calculated based on the total area of the droplets (Tab. 1 and 2)

**TABLE 1**
**SURFACE CONTAMINATION WITH DROPLETS OF CHLORIDE SOLUTIONS**
**($gCl^-/m^2$)**

| Solution | Saturated | Diluted | | | |
|---|---|---|---|---|---|
| | | x3 | x10 | x30 | x100 |
| NaCl | 200 | 67 | 20 | 6.7 | 2 |
| $MgCl_2$ | 344 | 115 | 34.4 | 11.5 | 3.4 |

All specimens deposited with salts were exposed in the environmental chamber for one month (~720h) with the relative humidity (RH) steps of 10% to each test (from 40% RH up to 70% RH). The testing temperatures were controlled at 40°C and 70°C.

**TABLE 2**
**DIAMETERS OF CHLORIDE DROPLETS AREA ON THE U-BEND SPECIMENS (mm)**

| U-bend specimen | Diameter of six droplets (mm) | | | |
|---|---|---|---|---|
|  | φ1 | φ2 | φ3 | Ave |
| | 2.82 | 5.37 | 2.60 | 3.59 |
| | φ4 | φ5 | φ6 | |
| | 2.81 | 4.73 | 3.21 | |
|  | φ1 | φ2 | φ3 | Ave |
| | 2.84 | 3.96 | 3.68 | 3.57 |
| | φ4 | φ5 | φ6 | |
| | 2.77 | 4.15 | 4.00 | |

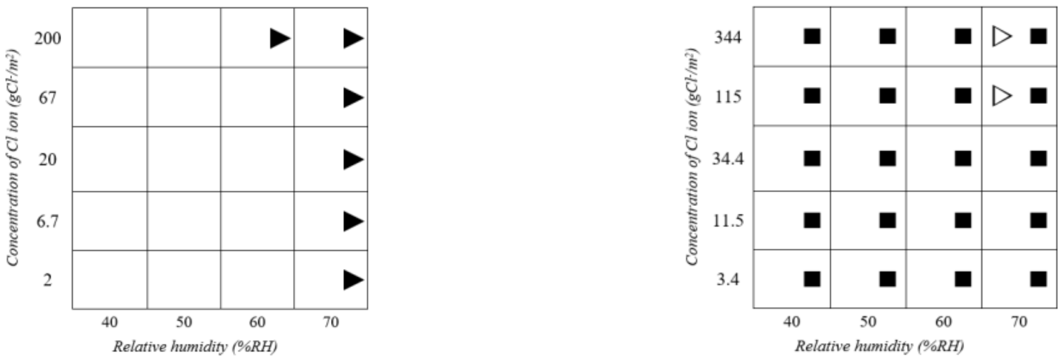
## 2.3 Optical and scanning electron microscopy

After exposure, the samples were washed in distilled water to remove the remaining salt and any loosely-attached corrosion products, then cleaned in acetone and dried by hot air. The tested samples were firstly observed under a optical microscope (Axiovert 40MAT- Carl Zeis) and the pit depths were measured. The Scanning Electron Microscopy (JEOL-JSM 6490) was used to identify the SCC cracks and to observe the morphology of the SCC cracks.

# III. RESULTS AND DISCUSSION

## 3.1 The flat samples

All samples deposited with various concentration of chloride ions were exposed in the environmental chamber at 40$^o$C and 70$^o$C which combined with four different levels of 40%, 50%, 60% and 70% RH. The tests were terminated after 30 days exposure. The results for type 304 as-received flat samples are presented in Fig 3.




a/ NaCl
▷ pit-40$^o$C
► pit-70$^o$C

b/ $MgCl_2$
□ surface crack-40$^o$C
■ surface crack-70$^o$C

**FIGURE 3. The corrosion behavior of the as-received flat samples deposited with saturated NaCl droplets (a) and $MgCl_2$ droplets (b)**

It is recognized that concentrated NaCl solutions were not severe enough for SCC occurred on the type 304 as-received flat samples at 40$^o$C. Even at the high temperature (70$^o$C), only pitting was observed at 70% RH (Fig.3.a).

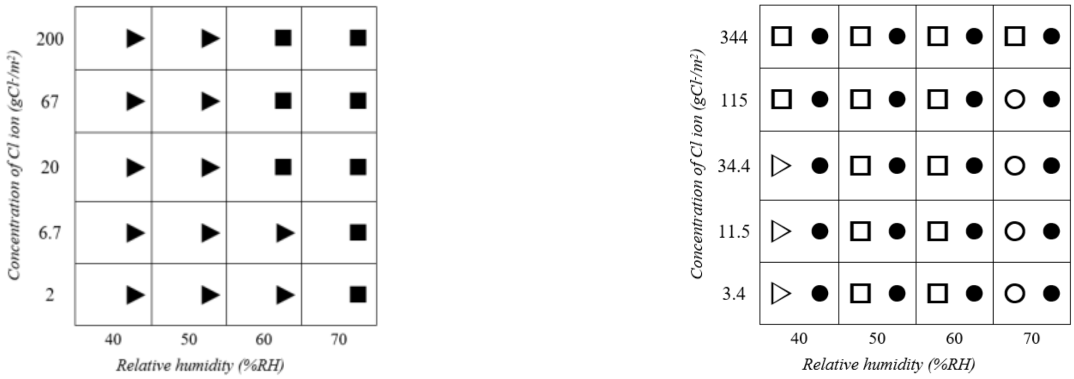
For the $MgCl_2$ deposited samples, almost no failure occurred at 40$^o$C, but only pitting corrosion appeared at 70%RH on the samples deposited with high chloride levels – saturated and three times diluted. (Fig.3b and 4a). At 70$^o$C, the cracks appeared on all the samples, irrespective of values of relative humidity and concentration of chloride ion, the pit size was larger and the cracks initiated from the pits were observed (Fig. 3b and Fig. 4b). The above results can be explained as follows: The chloride amount in one droplet of $MgCl_2$ solution is always higher than that in one droplet of NaCl solution, in addition, $MgCl_2$ solution is acidic (with pH = 5.7), which accelerated the metallic soluble react. Because $MgCl_2$ deliquesced at lower

RH in comparison to NaCl, the corrosion easier occurred on the samples deposited with $MgCl_2$ at the low RH (as 40, 50 and 60%) while no corrosion appeared on the samples deposited with NaCl at the same RH.

a/ 40°C, 70%RH b/ 70°C, 70%RH

**FIGURE 4. The appearance of the as-received flat samples with saturated $MgCl_2$ droplets after 30 days, (160x)**

The results of testing the sensitized flat specimens are given in Fig. 5, which shows higher SCC susceptibility than that of the as-received specimens due to depletion of Cr in the area near the grain boundary.

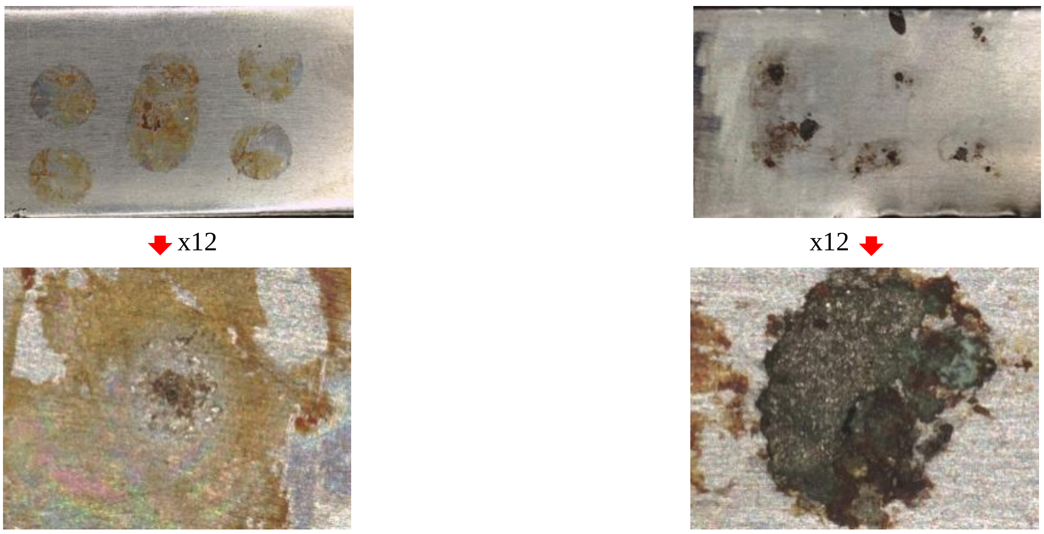



a/ 40°C, 70%RH b/ 70°C, 70%RH

▷ pit-40°C □ surface crack-40°C ○ SCC-40°C

▶ pit-70°C ■ surface crack-70°C ● SCC-70°C

**FIGURE 5.The corrosion behavior of the sensitized flat samples with NaCl droplets (a) and $MgCl_2$ droplets (b)**



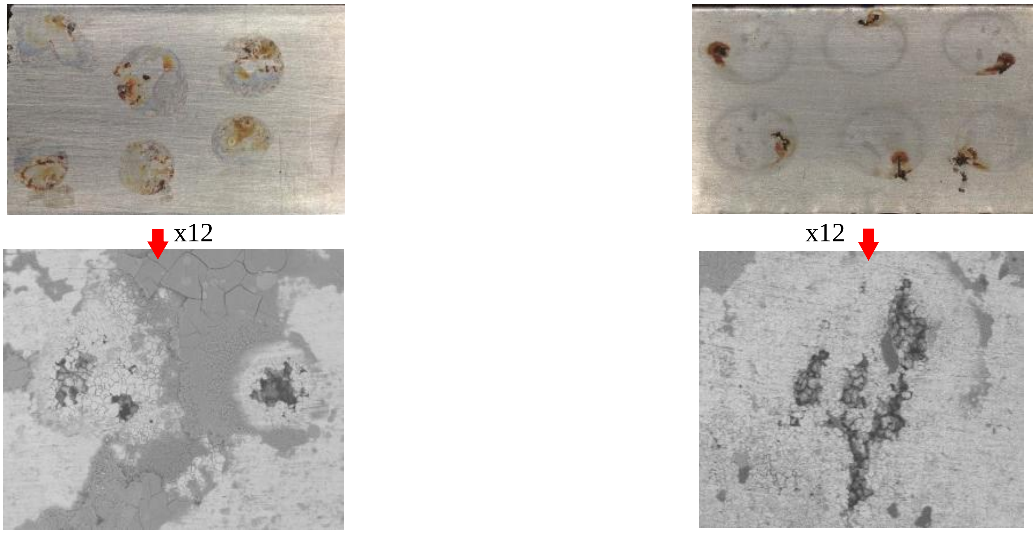

x160 x160

a/ NaCl, 70°C, 40%RH b/ NaCl, 70°C, 70%RH

**FIGURE 6. The appearance of the sensitized flat samples with saturated solution NaCl droplets**

Similar to the as-received samples, the NaCl droplets does not cause SCC of the material at 40$^oC$; however, at the higher temperature (70$^oC$), the pits were formed on the surface of all the samples tested at 40% and 50% RH. At 60% RH, the surface crack was observed on the samples deposited with NaCl of at least 20gCl/m$^2$. At 70% RH, the SCC cracks appeared on all samples tested at every NaCl concentration. Therefore, NaCl is easier deliquesced at higher RH, which accelerated the metallic soluble react at the crack tip and promoted the cracks appeared. The increase of temperature and $Cl^-$ content also showed the similar promotion as the above.

With regard to the sensitized flat samples deposited with $MgCl_2$, the pits and shallow SCC crack were observed more severely than those dropped with NaCl, which is indicated by the larger SCC cracking size (Fig. 5.b). The pits and the surface cracks were found right at low temperature (40$^oC$) and low RH (40, 50, and 60%) (Fig. 7a); at 70$^oC$, SCC propagation appeared at all samples regardless the values of RH (Fig. 5b and 7b). By means of the increasing temperature and RH, the SCC initiated and the number of crack as well as the crack length becomes greater.




a/ $MgCl_2$, 40$^oC$, 70%RH　　b/ $MgCl_2$, 70$^oC$, 70%RH

**FIGURE 7. The appearance of the sensitized flat samples with saturated solution of $MgCl_2$ droplets**

***The main observations*:** At low temperature, the initiation and the development of SCC in stainless steels was mainly controlled by the concentration chloride ion and the relative humidity. And it's required more than 30 days for the development of SCC from the pitting. Otherwise, at high temperature, corrosion mode transformations were more rapidly.

### 3.2 The test of the U-bend samples

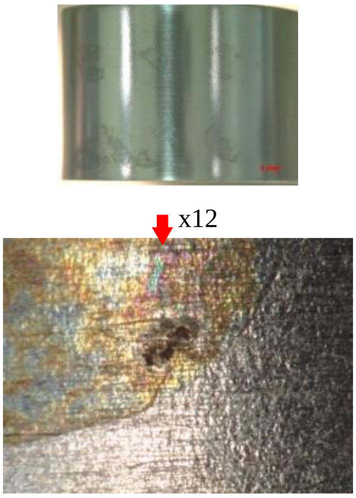
Following the flat sample trials, the U-bent samples were tested in the same conditions with those applied to the flat samples. The corrosion behaviors of the as-received U-bend samples are expressed in Fig. 8.


a/ 40$^oC$, 70%RH　　b/ 70$^oC$, 70%RH

▷ pit-40$^oC$　□ surface crack-40$^oC$　○ SCC-40$^oC$

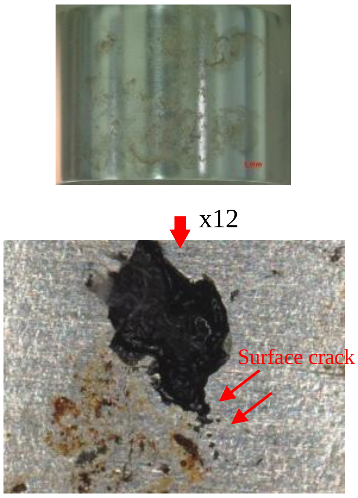
► pit-70$^oC$　■ surface crack-70$^oC$　● SCC-70$^oC$

**FIGURE 8.The corrosion behavior of the as-received U-bend samples with NaCl droplets (a) and $MgCl_2$ droplets (b)**




x160

a/ NaCl, 70$^o$C, 50% RH



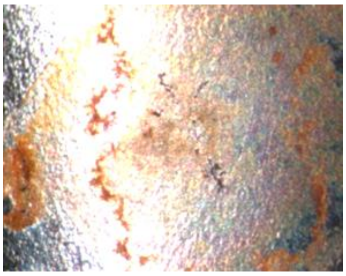

x160

b/ NaCl, 70$^o$C, 70% RH

**FIGURE 9. The appearance of the as-received U-bend samples with saturated solution of NaCl**

Similar to the pattern of the as-received flat samples deposited with NaCl, there was no evidence of corrosion on the as-received U-bent samples at 40$^o$C. The pits and surface cracks appeared only on the samples exposed at 70$^o$C combined with 60 and 70% RH, however, the pits were also observed at 50% RH on the sample deposited with saturated and three times diluted chloride solution (from 67 to 200 $gCl^-/m^2$), see Fig.8a. and 9b.

With respect to the as-received U-bent samples deposited with $MgCl_2$ and tested at 40$^o$C, the pits and cracks as well as SCC were observed only at the chloride content ≥34.4gCl-/$m^2$ which perhaps are considered as the critical chloride level for the pits occurred at low temperature. Almost samples tested at 70$^o$C showed SCC cracks, regardless of either the chloride content or the value of RH. After testing, the fracture appeared on the surface of all specimens (Fig.10).



a/ 40$^o$C, 50%RH

b/ 70$^o$C, 70%RH

**FIGURE 10. The appearance of the as-received U-bend samples with saturated solution of $MgCl_2$ droplets (160x)**

For specified combinations of low temperature and low relative humidity (40°C, 40% of RH), the pits and surface SCC cracks were also appeared on the as-received U-bend samples deposited with $MgCl_2$ saturated solution(Fig. 8b and 11).

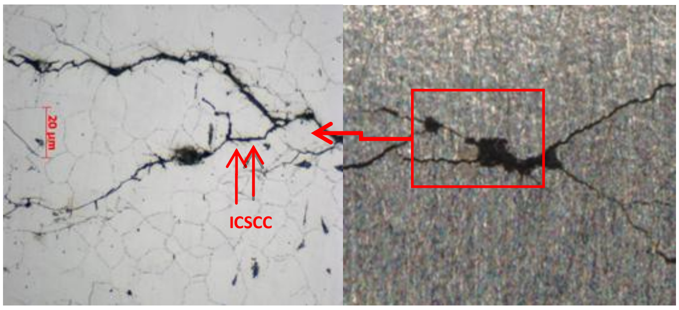
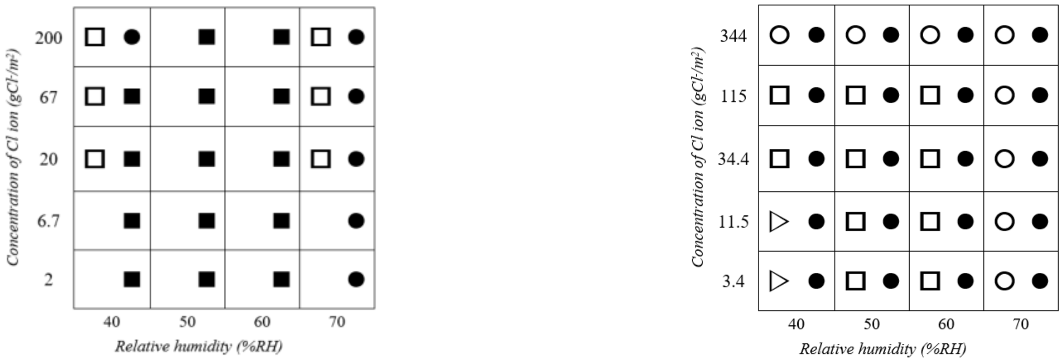



**FIGURE 11. Morphology of crack on U-bend sample type 304 ($MgCl_2$ saturated solution, 40% of RH and 40°C)**

This suggested that at the low relative humidity, the layer of droplets solution was thinner than the one's at high relative humidity. The oxygen is easier to attack the surface of material. A combination of ion chloride in the test solution at the high potential on the surface of samples, the SCC initiation was observed. The crack appeared and grew from pit to pit on the specimen surface. The SEM confirmed that the crack most often propagated by inter-granular path.

The results of testing the sensitized U-bend samples are shown on Fig. 12. For the specimens dropped with NaCl and tested at 40°C, the surface cracks were found at 40% and 70% RH when the minimum of chloride ion level is ≥20 $gCl^-/m^2$(Fig. 12a and 13a).

Under the condition of higher temperature (70°C), the surface crack was observed on all the specimens tested at 40, 50 and 60% RH without distinction of concentration of chloride ions. Furthermore, when the RH increased, the SCC crack was found to propagate and the secondary crack was very easily detected (Fig.12a and 13b).




a/ 40°C, 70%RH b/ 70°C, 70%RH

▷ pit-40°C □ surface crack-40°C ○ SCC-40°C

► pit-70°C ■ surface crack-70°C ● SCC-70°C

**FIGURE 12. The corrosion behavior of the sensitized U-bend samples with NaCl droplets (a) and $MgCl_2$ droplets (b)**

a/ 40°C, 70%RH b/ 70°C, 70%RH

**FIGURE 13.The appearance of the sensitized U-bend samples with saturated solution of NaCl droplets (12x)**

In the experiments of U-bend specimens with $MgCl_2$ droplets, the SCC-accelerated was not controlled by the humidity of environment. The main factors which influence SCC were the temperature and concentration of chloride ions (Fig. 12.b).

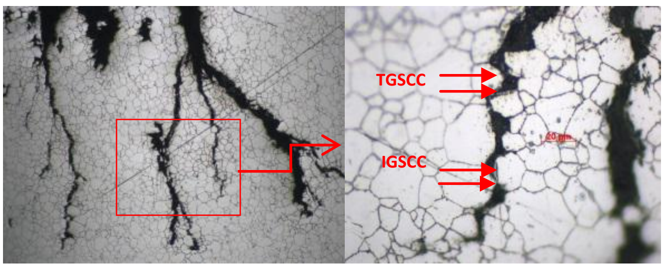



**FIGURE 14. Morphology of the crack on U-bend sample type 304 ($MgCl_2$ saturated solution,40% of RH and 40°C)**

At low temperature (40°C), the severity of SCC is controlled by the increase of RH and chloride ion content. Under the saturated $MgCl_2$ droplets SCC cracks were found on all samples, irrespective of the RH values, and at 70%RH, the SCC cracks appeared regardless of the chloride ion content. In addition, the SCC cracks were also found to develop from the pits

on the sensitized specimens exposed to $MgCl_2$ at low RH (40% and 50% of RH). The crack often propagated by the inter-granular and trans- granular path (Fig. 14.).

Finally, at 70$^o$C, the SCC cracks were observed on all of specimens, irrespective of RH values or ion chloride concentration (Fig. 12b). Especially the samples with saturated MgCl2 solution, which were tested at 70oC and 70%RH, were broken completely. The high humidity and high temperature as well as high chloride concentration may accelerate the metal soluble react at the crack tip, which speeds the crack propagation (Fig.15 b).

a/ 40$^o$C, 70%RH

b/ 70$^o$C, 70%RH

**FIGURE 15.The appearance of the sensitized U-bend samples with saturated solution of $MgCl_2$ droplets (12x)**

Similar to the case of flat samples, the $MgCl_2$ showed the more severe SCC to type 304 stainless steel than NaCl did; The severity of SCC is increased with the increase of RH and $Cl^-$ concentration; And the temperature accelerated the SCC stronger occurred. All the explanations are the same those given above.

## IV. CONCLUSION

The sensitized samples are more susceptible with SCC in comparison with the as-received samples (cold work). The U-bend samples are more susceptive with SCC than the flat samples.

With 30 day-exposure at low temperature (40$^o$C), NaCl did not result in SCC on the as-received samples; however, the saturated NaCl caused the surface crack on the sensitized U bend sample at the condition of 40$^o$C and 40%RH. $MgCl_2$ is more active; it caused the pitting corrosion, the surface cracks or SCC propagation on almost samples. At the high temperature (70$^o$C), both NaCl and $MgCl_2$ caused pitting corrosion, surface crack, or SCC initiation.

The increase of temperature, RH as well as chloride concentration promoted the pitting corrosion as well as accelerated the metal soluble react at the crack tip and foster SCC propagation.

The exposure test should be extended for further understand the impact of NaCl on SCC susceptibility of type 304 stainless steel.

## REFERENCES

[1] M.P. Ryan, D.E. Williams, R.J. Chater, B.M. Hutton, D.S. McPhail, "Why stainless steel corrodes", Nature 415 (2002) 770–774.

[2] S. Lozano-Perez, J. Dohr, M. Meisnar, K. Kruska, "SCC in PWRs: learning from a bottom-up approach", Metall. Mater. Trans. E 1 (2014) 194–210

[3] Turnbull, L.N. McCartney, S. Zhou, "Modelling of the evolution of stress corrosion cracks from corrosion pits", Scr. Mater. 54 (2006) 575–578

[4] Turnbull, L.N. McCartney, S. Zhou, "A model to predict the evolution of pitting corrosion and the pit-to- crack transition incorporating statistically distributed input parameters", Corros. Sci. 48 (2006) 2084–2105

[5] J.E. Truman, Corrosion Science 17 (1977) 737–746

[6] J.i. Tani, M. Mayazumi, N. Hara, "Stress corrosion cracking of stainless steel canister for concrete cask storage of spent fuel", J. Nuci. Mater. 379 (2008) 42-47.

[7] Phan, D. "Atmospheric – Induced Stress corrosion cracking of Austenitic stainless steel" PhD thesis, University of Manchester, Manchester, UK, (2009).

[8] Cook, N. P. Stevens, and J. Duff, "Atmospheric corrosion of nuclear waste containers" DIAMOND' 10 Conference Decommissioning, Immobilization and Management of Nuclear Waste for Disposal, Manchester, (2010).

[9] H.E. Hannien, "Influence of metallurgical variable on environment-sensitive cracking of austenitic alloys", Int. Mater. Rev. 24 (1979) 85-136.

[10] ASTM G30-97: Standard Practice for making and Using U-Bend Stress-Corrosion Test Specimens.